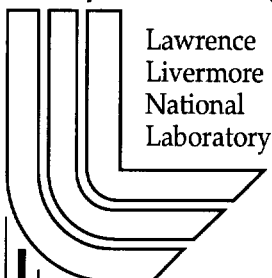# Direct Carbon Conversion: Review of Production and Electrochemical Conversion of Reactive Carbons, Economics and Potential Impact on the Carbon Cycle

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Abstract

Concerns over global warning have motivated the search for more efficient technologies for electric power generation from fossil fuels. Today, 90% of electric power is produced from coal, petroleum or natural gas. Higher efficiency reduces the carbon dioxide emissions per unit of electric energy. Exercising an option of deep geologic or ocean sequestration for the CO_2 byproduct would reduce emissions further and partially forestall global warming.

We introduce an innovative concept for conversion of fossil fuels to electricity at efficiencies in the range of 70-85% (based on standard enthalpy of the combustion reaction). These levels exceed the performance of common utility plants by up to a factor of two. These levels are also in excess of the efficiencies of combined cycle plants and of advanced fuel cells now operated on the pilot scale.

The core of the concept is direct carbon conversion a process that is similar to that a fuel cell but differs in that synthesized forms of carbon, not hydrogen, are used as fuel. The cell sustains the reaction, $C + O_2 = CO_2$ ($E \sim 1.0$ V, T = 800 ¡C). The fuel is in the form of fine particulates ($\sim$100 nm) distributed by entrainment in a flow of CO_2 to the cells to form a slurry of carbon in the melt. The byproduct stream of CO_2 is pure. It affords the option of sequestration without additional separation costs, or can be reused in secondary oil or gas recovery. Our experimental program has discovered carbon materials with orders of magnitude spreads in anode reactivity reflected in cell power density. One class of materials yields energy at about 1 kW/m^2 sufficiently high to make practical the use of the cell in electric utility applications.

The carbons used in such cells are highly disordered on the nanometer scale (2-30 nm), relative to graphite. Such disordered or turbostratic carbons can be produced by controlled pyrolysis (thermal decomposition) of hydrocarbons extracted from coal, petroleum or natural gas. For coal and lignite, such hydrocarbons may be produced by cyclic hydrogenation (hydropyrolysis), with the recycle of the hydrogen intermediate following pyrolysis. Starting with common CH_x feedstock for carbon black manufacture, the ash entrained into the carbon ($<$0.03%) does not jeopardize cell life or enter into the economic estimates for power generation.

The value of carbon (relative to hydrogen) as an electrochemical fuel derives from thermodynamic aspects of the C/O_2 reaction. First, the entropy change of the C/O_2 reaction is nearly zero, allowing theoretical efficiencies ($\Delta G(T)/\Delta H_{¡298}$) of 100 % (cf. H_2/O_2 theoretical efficiency of 70%). Second, the thermodynamic activity of the carbon fuel and the CO_2 product are spatially and temporally invariant. This allows 100% utilization of the carbon fuel in single pass (cf. hydrogen utilizations of 75-85%). The carbon/melt slurry is non-explosive at operating temperatures. The total energy efficiency for the C/O_2 is roughly 80% for cell operation at practical rates.

In summary, what gives this route its fundamental advantage in energy conversion is that it derives the greatest possible fraction of energy of the fossil resource from an electrochemical reaction ($C+O_2 = CO_2$) that is comparatively simple to operate at efficiencies of 80%, in a single-pass cell configuration without bottoming turbine cycles.

System efficiency estimates were conducted for several (existing) routes involving (1) extraction of a hydrocarbon from the fossil resource by (hydro) pyrolysis, (2) thermal decomposition to a reactive carbon, followed by (3) conversion of the carbon and byproduct hydrogen in (separate) fuel cells. The global energy efficiencies of the process were estimated to be (1) 80-85% HHV for direct conversion of petroleum coke; (2) 67% HHV for pyrolysis of

CH_4; (3) 72% HHV for pyrolysis of heavy distillates (modeled using properties of decane); (4) 75.5% HHV (83% LHV) for natural gas conversion with a Rankine bottoming cycle for the hydrogen portion; and (5) 69% HHV for conversion of low rank coals and lignite through hydrogenation of the solid fuel and pyrolysis of the methane intermediate, again with a bottoming cycle for the hydrogen conversion step.

The costs of the processes are estimated from the costs of industrial production of carbon blacks from the feedstock of methane and various petroleum cracking fractions. Carbon blacks are produced by a long sequence of unit processes, the first of which is thermal decomposition. The cost of this first step, which determines fully the nanostructure and reactivity of the carbon fuel, is 9-11 cents/lb ($7/GJ based on combustion energy). (Subsequent stages of quenching, separations, chemical treatments, bagging, etc., are not needed in the proposed combined pyrolysis and electric power plants). Electrode grade petroleum cokes cost in the range of 1-6 $/GJ. Steam-reformed hydrogen, by comparison, is about $7/GJ (1999 NG prices). At $0.10/kWh, the cost of electricity corresponds to $27/GJ.

The currently rising prices of natural gas (now at $7/GJ, or $7.50/MBTU; December 2000) will tend to inflate the costs of carbon blacks as well as steam-reformed hydrogen.

The cost of the cell can be estimated from the current design of laboratory cells. Using a planar configuration with nickel felt air electrode, zirconia fabric separator, nickel felt anode current collector and graphite and stainless steel construction, the cost of the cell is estimated to be below $500/kW.

The reduction achieved by implementation of such technologies on carbon dioxide emissions is inversely proportional to the increase in efficiency (a factor of 1.8-2). The marginal decrease in CO_2 emissions is 50% relative to current technologies. If the option for sequestration is exercised for only the byproduct of the cell (pure CO_2), then carbon dioxide emissions are decreased by roughly a factor of 10 per unit of electric energy.

We believe this technology to be a favorable option for conversion of any fossil fuel to electricity. The advantages increase as the fraction of carbon in the fossil fuel increases. Since coal comprises over half of the world s fossil resources (81% of which resides in North America, Former Soviet Union or China), it is particularly important that advanced technologies for coal conversion be examined to provide technically and economically attractive incentives to international cooperation.

Critical steps in the development of the technology for fossil energy conversion through direct carbon fuel cells include: (1) Extended duration tests of the cell on an engineering scale (1 kW) using a pneumatic feed of carbon fuel; (2) Development of a scientific theory allowing prediction of carbon electrochemical and chemical activity on the basis of measurable parameters of structure, and relation of such structure to the conditions of pyrolysis; (3) Examination of certain electrolyte compositions allowing the conversion of high-sulfur petroleum cokes; and (4) detailed examination of alternative means of extraction of hydrocarbons from coal and lignite by pyrolysis, hydro-pyrolysis or solvent extraction.

This report contains the abstract and executive summary of the final report for a study sponsored by the Lawrence Livermore National Laboratory Council on Energy and Environmental Systems (May-October 2000). The supporting text and a number of appendices containing proprietary information will be published separately.

Executive Summary

1. Introduction

The progressive buildup of heat-retaining gases in the atmosphere may well be responsible for long-term global warming trends [1,2]. The threat of irreversible global warming has revitalized interest in development of very efficient electric power production from fossil fuels achieving conversion efficiencies far in excess of those demonstrated by today s electric utilities. Advanced technologies for CO_2 collection, separation and geologic sequestration are also subjects of active research and development.[3]

As a means of reducing greenhouse-gas emissions, we introduce an innovative concept for conversion of fossil fuel resources into electricity at very high efficiencies in the range of 70-85% (based on the heat of oxidation of the primary fuel, ΔH^0_{298}). This concept entails the following sequence: (1) extraction of hydrocarbons from fossil fuels; (2) thermal decomposition into elemental carbon and hydrogen gas, and (3) electrochemical conversion of the carbon and hydrogen in (separate) fuel cells. The direct carbon conversion cell, or carbon fuel cell, uses a molten salt electrolyte at 750-850 ¡C and supports the net reaction, $C + O_2 = CO_2$. We use highly reactive turbostratic carbons formed by pyrolysis of various hydrocarbons derived from fossil fuels. These carbons deliver >0.8 V at 0.5- to 1 kA/m². At 0.8 V, the efficiency is ~80% of heat of combustion of carbon. Electrochemical and systems aspects have been reported in open literature as well as in records of invention. [4-10].

We believe this approach to be capable of converting many fossil fuel resources into electric power at total efficiencies of 70-85% (HHV) a significant improvement over the level achieved in advanced fuel cells and combined cycle plants (45-55%, HHV) and more broadly applicable by being able to link to *any* fossil carbon resource, through extraction and pyrolysis of CH_x. The overall process is depicted in Figure 1.
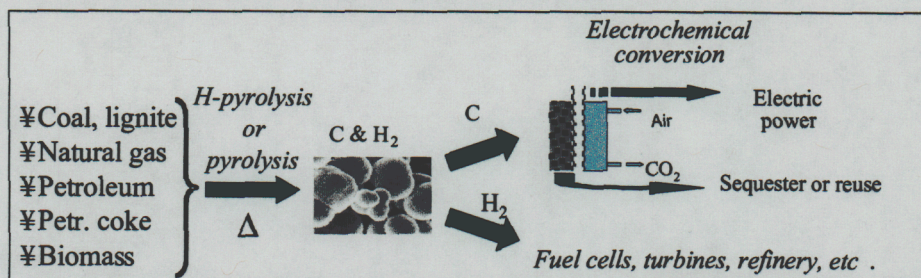

Fig. 1. We are investigating the sequence for electric power generation: (1) extraction of CH_x, (2) pyrolysis to C and H_2, and (3) conversion in separate fuel cells. The pure CO_2 product may be sequestered or reused in enhanced oil or gas recovery.

2. The Direct Carbon Conversion Cell.

The new technology in this approach is the direct carbon conversion cell. It uses a slurry of carbon particles in a molten salt. Carbon black particles (typically, 30-100 nm size) are distributed by entrainment in a CO_2 carrier gas into one chamber of the electrochemical cell. (Fig. 2). A pure CO_2 product gas is evolved from the anode chamber. Some CO_2 diffuses across the thin separator to react with atmospheric oxygen to balance the cathodic reaction.

Using highly reactive turbostratic carbons produced by rapid thermal decomposition of hydrocarbon oils, we have demonstrated cells yielding 0.8 V at 1 kA/m² rates sufficient for practical operation of large generating units (Figure 3a). (This rate is about half of that used by

the Westinghouse tube SOFC operating at the same voltage and producing a power density of about 1.5 kW/m^2, as shown in Fig 3b. [see ref 11, p. 5-16]) We expect further research to yield carbon fuels affording significantly higher discharge rates.
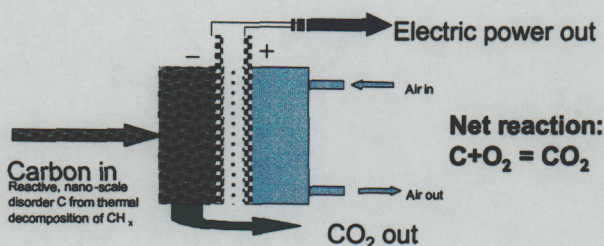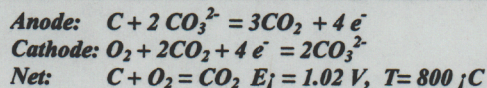

Net reaction:
$C+O_2 = CO_2$

Fig.2. A direct carbon conversion cell, or carbon fuel cell, reacts particulate carbon with atmospheric oxygen in a cell with a molten salt electrolyte at 750-850 ¡C

Anode: $C + 2\ CO_3^{2-} = 3CO_2 + 4\ e^-$
Cathode: $O_2 + 2CO_2 + 4\ e^- = 2CO_3^{2-}$
Net: $C + O_2 = CO_2\ \ E_¡ = 1.02\ V,\ \ T = 800\ ¡C$

The pneumatic transport of carbon fines through complex unit process equipment is practiced by the thermal-black and furnace black industries on scales of several million tons per year. In our application, a minute part of the CO_2 offgas (<0.03%) would be fed back to entrain and distribute carbon fuel fines.

An excellent review of the literature on carbon structures, pyrolysis and manufacturing has been published [12].
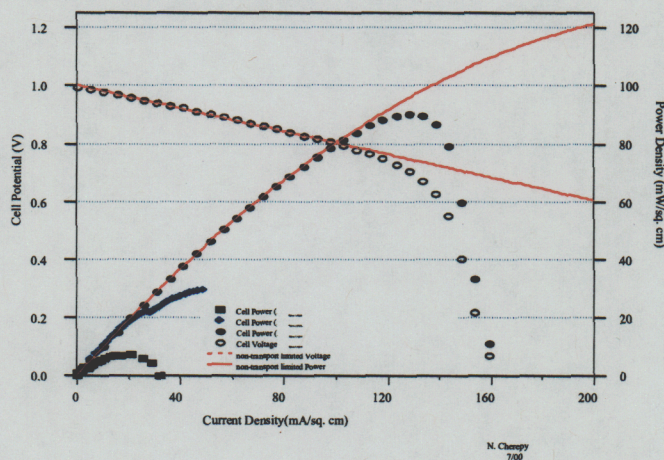

Fig. 3a. Polarization and power curves are shown for three different samples of carbon produced by pyrolysis. These carbons are produced by the same fundamental process (thermal or oxidative decomposition) and differ only in the nature and degree of disorder on the nanometer scale.
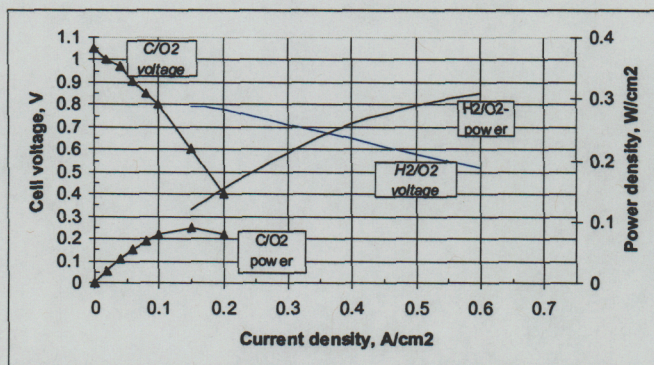

Fig. 3b. Specific power achieved by the C/air cell is not greatly lower than that achieved by the Westinghouse technology (3 ATM; 85% utilization), when the comparison is made at the voltage of intended operation (0.8 V, ~ 80% voltage efficiency. (ref. [11]).

3. Thermodynamic basis for enhanced efficiency through carbon conversion

Any hydrocarbon oil or gas (represented by CH_x) can be readily decomposed into a turbostratic carbon and hydrogen a process that consumes a small fraction (3-9%) of the heat of combustion of the hydrocarbon. The technical approach of hydrocarbon pyrolysis and conversion C and H_2 in separate fuel cells has fundamental advantages:

- The free energy (ΔG_{iT}) and the standard enthalpy (ΔH_{i298}) of the C/O_2 reaction are nearly identical, allowing theoretical efficiencies of 100%, (cf. 70% for H_2/O_2). The entropy change is essentially zero. (ΔS = +0.7 e.u./4-equiv.; c.f. ΔS = - 21 e.u./4-equiv for H_2/O_2).
- The EMF, or theoretical driving force for the cell, is independent of position within the cell and independent of the extent of conversion of the carbon fuel a consequence of invariant thermodynamic activities and separated phases for C and CO_2. This allows carbon utilization approaching 100%, in single pass operation, and without sacrificing the high rate of discharge. (Hydrogen utilization is commonly ~80%) (Fig. 4)
- The near-zero entropy change of the reaction minimizes heat rejection requirements and eliminates large and non-uniform thermal loads on the cell.
- The C/molten-salt slurry does not explode if inadvertently brought in contact with air at 750-850 ¡C a fact which allows thinner, more flexible separators with lower electrical resistance and consequent power losses. Engineering design for explosion mitigation is avoided.
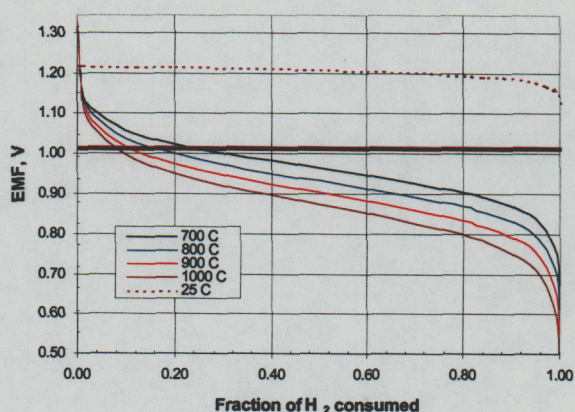

Fig 4. The driving force for electrochemical power generation, or EMF, depends on temperature, extent of reaction and position in the cell for high-temperature H_2/O_2 cells, but is invariant for C cells (T = 700-900 ¡C, solid, horizontal line) and nearly constant for a low temperature PEM fuel cell (broken line). Invariance allows full utilization of the carbon fuel.

The electrochemical efficiencies of various fuel cells are compared in Table 1. The actual operating efficiency of a fuel cell is a consequence of the balance of economics, technology limits and practical design choices. Nonetheless, electrochemical engineers commonly represent the net efficiency of a fuel cell as the product of three terms:

$$Net\ efficiency = (\Delta G_T/\Delta H_{298})\ x\ (fuel\ utilization\ factor)\ x\ (V(i)/E_i)$$

The carbon cell combines a high theoretical efficiency (100.3%) with 100% utilization (single pass mode) and high voltage efficiencies for a net efficiency of 80% (based on ΔH_{i298} for C/O_2). The analysis of efficiency in this report parallels the derivations given in Liebhafsky and Cairns [13] and Burger [14].

Table 1. Comparison of efficiencies of fuel cells using synthetic or refined fuels. Operating temperature = 750 ¡C. Energy cost of fuel synthesis is excluded.

Fuel	$\Delta G/\Delta H_{i298}$	fuel utilization factor	Voltage efficiency, $V(i)/E_i$	Net efficiency
C	1.003	1.0	0.8	0.80
H_2	0.70	0.75-0.85	0.8	0.42-0.48
CH_4[a]	0.89	0.75-0.85	0.8	0.53-0.60

[a]Assumes perfect internal steam reforming reaction. Direct electrochemical discharge of methane at a catalyzed surface does not occur at measurable rates. (See discussion [11] and review [15])

To summarize, what gives the proposed route its unique advantages in energy conversion is that it derives the greatest fraction possible of the fossil fuel energy from an electrochemical reaction ($C + O_2 = CO_2$) that is comparatively simple to operate at efficiencies that can approach 100%.   The simplicity derives from three sources: (1) There is no need to collect and recycle waste entropy heat. (2) All the carbon is consumed to make electricity in a cell with spatially and temporally constant voltage and current density. (3) The pyrolysis of hydrocarbons consumes less energy and requires less capital than steam reforming or syngas production.

Historical perspective: actual hydrogen fuel cell efficiencies. The actual efficiencies of advanced power sources are given in Table 2, and represented graphically in the chart (Fig. 5). Figure 5 assumes that methane derived from natural gas is the fuel for all of the processes listed, with a vaporous water product. Hence, efficiencies are given in terms of LHV. We have added a separate ordinate to express efficiency in terms of standard heat of combustion, which has universal meaning for any fuel. For saturated hydrocarbons, the HHV or ΔH^0_{298} is typically about 10% greater than the LHV. In Figure 4, the added ordinate referenced to ΔH^0_{298}, is shifted a uniform 10% relative to the LHV. For carbon, only the standard heat of reaction, ΔH^0_{298}, has meaning, as no water is involved. [A further requirement for reference potential might specify the partial pressure for oxygen, but fuel cells differ in their optimum cathode gas compositions.]

Advanced combined cycle plants operating on methane will operate at about 50% efficiency HHV (56% LHV).

Table 2. Energy conversion efficiencies of piloted or projected fuel cell systems [11].

Type	Implementation	Efficiency	
		% LHV	% HHV
Phosphoric acid	Deployed 200 kW units (PC25, United Technologies); reformed hydrocarbons	37-42	~ 36
Molten carbonate	ERC pilot, 2 MW; externally reformed hydrocarbons or coal	44-49	40-45
	ERC 2.8 MW commercial prototype; Internally reformed CH_4	58	~52
	MC Power, 275 kW, externally reformed	44.4	~39
	MC Power, 275 kW, externally reformed; 3 Atm. 650 ¡C; commercial in 2002	54	~49
Solid oxide	Siemens/Westinghouse 25- and 100 kW systems; $CO + H_2$	45-50	~42
	Siemens/Westinghouse; 25- and 100 kW; hybrids with turbine	~60	~54
Vision 21	Goal of multistage, high pressure SOFC	66	60

Source: National Energy Technology Laboratory, *Fuel Cell Handbook* Nov. 1998.[11] Values for HHV are approximate, and calculated as 0.9 x LHV for methane.
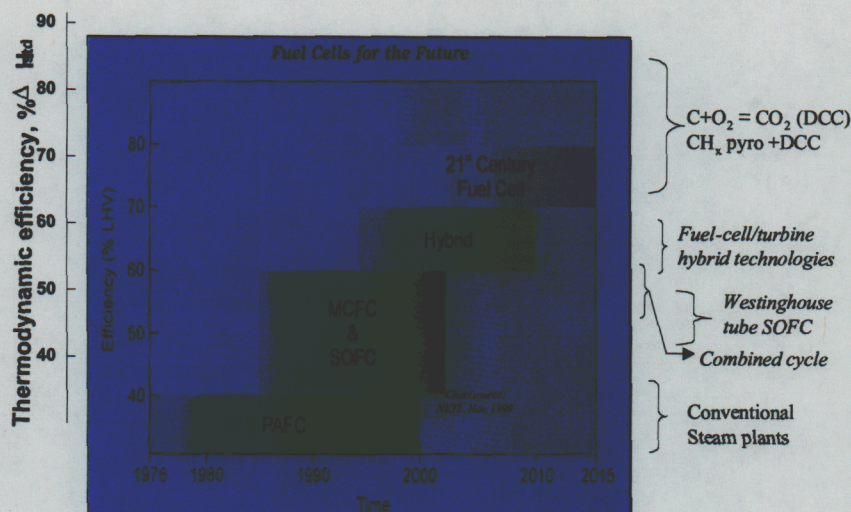

Fig 5. Fuel cells for the future are summarized in this chart from National Energy Technology Laboratory (1998). We have added a separate ordinate scale for standard heat of combustion, $\Delta H_{f\,298}$, and the approximate values of advanced power generation techniques.

4. The structural and purity requirements of a carbon fuel

The materials requirements placed on carbon fuels derive primarily from factors of crystallographic structure (measured on the 2-30 nm scale) and to a lesser extent from specific surface area of the microparticles. The relation of structure, form and surface area to reactivity in air oxidation is reviewed by Kinoshita [18].

Electrochemically unreactive impurities do not play, as far as we know, any significant role. Most carbon blacks contain a residual ash (from cat crackers or pyrolyzer vessel

degradation) of about 0.02-0.05 %. This has no effect on system performance, cost or life. A carbon/air cell operating at 1 kW/m^2 will process 1 g-C/cm^2 over a time interval of 4 days. If this carbon entrains ash at the rate of 0.03 %, then the time constant for accumulating ash comparable in weight to the fuel is 4/0.0003 days [37 years]. This is long compared to the optimistic life of any high-temperature fuel cell hardware (10 years).

Sulfur entrainment within high-sulfur fuels is not likely to be a limiting factor. The carbon anode does not make use of noble-metal surface catalysis subject to poisoning by sulfur, and carbon cokes used in aluminum refining anodes have sulfur levels up to 2.5%. Sulfur is emitted as COS, which can be collected and decomposed by hydrolysis to form H_2S and CO_2. However, metal parts must be avoided in the anodic chamber, as sulfur promotes the corrosion of many metals and most stainless steels. An alternative to nickel is highly-graphitized carbon foams a conductive and chemically resistant material coupled with a heavier separator material and positive pressure on the air side to contain the COS.

This tolerance for sulfur is in contrast with the case of hydrogen fuel cells. Sulfur at ppm levels is to be avoided in hydrogen fuel cells, as it poisons the catalysts used for hydrogen anodic oxidation.

The industrial products closest to our requirements for fuels are the furnace and thermal blacks made from the following feedstock materials: methane, steam cracker oils and cat cracker oils, and coal-tar distillates. Principal metal impurities in petroleum-derived cokes are nickel and vanadium neither of which are electrochemically active. In all, the products of conventional furnace or thermal black processes are adequate in purity for use in direct conversion cells, and form a basis for the estimates of costs and process efficiencies. Table 3 lists approximate ash and sulfur contained in common feedstock materials used for making carbon blacks.

Table 3. Impurities in feedstock materials used in carbon black manufacture [12].

Feedstock	ash, %	S, %
Methane derived from NG	--	--
Steam cracker products: naphtha, gas oil	0.02	0.2
Cat cracker products: heavy petroleum fraction	0.05	2.1
Coal tar distillates	0.04	0.6

5. System Efficiencies: Fossil Resources to Electricity

The system efficiencies (conversion of fossil fuels to electricity) are estimated for five different schemes, using petroleum, natural gas, heavy oils and coal/lignite as resources. These approaches are summarized in Table 3-5. All systems exceed the efficiency goal corresponding to 70% LHV, which has been set for the 21st Century Fuel Cell. [17]

Petroleum coke. The first entry in Table 5 describes perhaps the simplest route to carbon conversion, starting with the petroleum coke as a byproduct from oil refining. This product represents 2-10% of petroleum crude. Part of this material is used as the anode fuel in the Hall process for making aluminum. Petroleum coke has both sulfur and ash components. If the coking process is adjusted to limit ash to < 0.1 %, entrainment of ash into the cell has no negative effect on system economics or cell life. The sulfur (typically 0.25-2.5% in Hall process cokes) is rejected as COS, which can be decomposed by hydrolysis into CO_2 and H_2S. The presence of sulfur requires that metal parts in the anode be replaced by conductive graphite, which is 1000-fold less reactive than turbostratic carbons under consideration. This approach requires control of

the coking process to minimize graphitization. The total efficiency of this process should be in the range of 80-85% of ΔH^0_{298}. [19]

Natural Gas, Pyrolysis and Fuel Cells Alone. Entry 2 of Table 5 gives a simple process for conversion of natural gas. The methane component is pyrolyzed using the unconsumed fraction of the hydrogen gas exhausted from the fuel cell operating at a utilization of 80%. This provides a high fuel cell voltage and the 20% unconsumed hydrogen provides sufficient heat to drive the pyrolysis process at 80% thermal efficiency (0.2x58.7 kcal/mole x 2 mole = 24 kcal). Enthalpy of the exhaust gas streams is recovered and used to preheat the fuels. The overall efficiency is high (67% HHV) and the process is simple, not requiring turbo charging or bottoming cycles.

Petroleum vacuum gas oil. This approach is perhaps the most straightforward extrapolation from current practice, as fuel oils normally used in carbon black production easily meet requirements for low ash and afford excellent control over the nanostructure of the product. Intermediate cracking fractions are common feedstocks for furnace black production. We have modeled the energy balance here using decane (for purposes of computational simplicity). The heat of pyrolysis is less than 4% of the fuel value of the oil. The hydrogen stream is used at 90% single pass efficiency in a fuel cell, with recovery of unconsumed hydrogen by condensation of steam. Enthalpy of the exhaust gas streams is recovered and used to preheat the fuels. The overall efficiency is about 74% HHV (77% LHV) the highest we have seen proposed for a simple system without bottoming cycles.

Natural Gas, Pyrolysis, Fuel Cells and Rankine Cycle. One of us (Steinberg) analyzed the generic system shown in Table 5 entry 4, which decomposes methane using natural gas thermal energy and entrains the carbon product directly into a molten salt in proximity to the cell. Hot exhausts are combined to boil water for a Rankine cycle generator. The assumptions of efficiencies associated with each component are given in Table 3.

The net efficiency of the system is the ratio of the electric power outputs to the sum of the thermal values (HHV) of all fuel inputs. This efficiency is then given by:

Efficiency = (85+76+27)/(213+23+13) = 75.5% HHV (83.4% LHV)

This is significantly more efficient than the simple pyrolysis process of Table 5 entry 2 but requires an increase in complexity to recover waste heat and hydrogen fuel for use in steam bottoming cycle.

Table 3. Methane, fuel cell and boiler: summary of component operating conditions and efficiencies

Unit	Pressure Atm	Temperature, ¡C	Efficiency, %
CH₄ decomposer	1-5	800-1000	80
C/air cell	1-5	750-1000	86.3
SOFC	1-5	1000	55.6 (90% utilization)
Boiler, Rankine cycle	70	600	38

Hydropyrolysis, Fuel Cell and Rankine Cycle. Steinberg also analyzed a system for conversion of brown coal to methane, followed by pyrolysis and recycle of the hydrogen. Process summary operating conditions and efficiencies are given in Table 4.
The overall reaction used in the computation is for lignite:

$$CH_{0.8}O_{0.22} = C + 0.18\ H_2 + 0.22\ H_2O$$
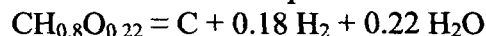
The net efficiency is the ratio of the electric power output (84.6 + 7.5 +5.9 kcal-e) to the thermal value of the inputs (1.27*113 kcal). This indicates a net efficiency of 69% HHV (76% LHV). This is the most efficient process yet proposed for coal.

Table 4. Parameters for the operation of a hydropyrolysis conversion of low-rank coal.

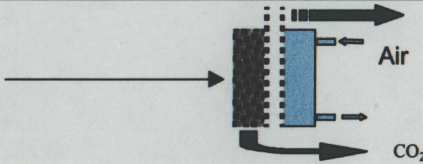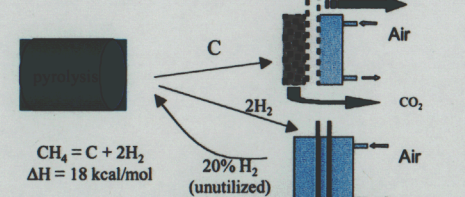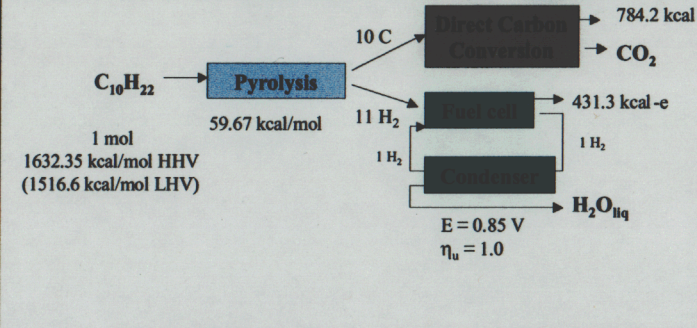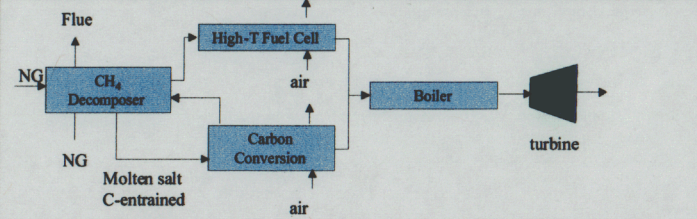| Unit	Pressure, Atm.	Temperature, ¡C	Efficiency
Hydropyrolyzer, fluidized bed	70	800-900	80
Methane decomposition to thermal black	1-5	900-1000	80
Carbon cell 84.6 kcal-e	1-5	750-1000	86.3
SOFC 7.5 kcal-e	5	1000	55.6
Boiler, Rankine Cycle: 5.9 kcal-e	70	600	38

Alternative Approaches. There are many intriguing approaches to fossil fuel conversion at very high efficiencies that we have not been able to discuss, given limitations in time and available open literature. The efficiencies and simplicities of the conversion processes (Table 5, entries 4,5) could probably be improved by eliminating the bottoming cycle, and use the enthalpy of the product gases and unconsumed hydrogen to offset process heat requirements for pyrolysis or hydropyrolysis reactions. The analysis is underway.

Professor Kas Hemmes and coworkers (Delft University of Technology, The Netherlands) are conducting research in a number of alternative carbon conversion systems [20-24]. In one approach, the carbon (or coke) is electrochemically oxidized to CO, and a very high cell voltage (relative to heat of combustion) is achieved. Because of the substantial entropy increase, the theoretical efficiency $\Delta G(T)/\Delta H_{std}$ exceeds 100% for the reaction, $C + \_ O_2 = CO$, with the entropy increase supported by heat absorption from solar or lower-grade fuel sources. The byproduct CO is then used in an electric turbine system, combusted for its thermal value, or used as a chemical process feedstock. Peelen et al. measured the polarization and complex impedance of the graphite electrode in molten carbonate melts, finding reasonably low anode resistances (12-60 Ω-cm^2) [23]. S. F. Au [24] analyzed the energy and exergy efficiencies of partial oxidation, direct carbon fuel cells, and internal direct-oxidation carbon fuel cells, showing high efficiencies when account is taken of the exergy of the high-temperature exhaust gas. This work references an earlier experimental and theoretical study of N. Nakagawa and M. Ishida [25], which treated the conversion of elemental carbon in a gas-phase solid oxide fuel cell, by driving the Boudouard reaction to regenerate *in situ* the electrochemically active intermediate CO, as shown in Figure 6:

$$C + CO_2 = 2\ CO \quad \text{(Boudouard reaction)}$$
$$2CO + O_2 = 2CO_2 \quad \text{(Electrochemical conversion)}$$
$$C + O_2 = CO_2 \quad \text{(Net)}$$
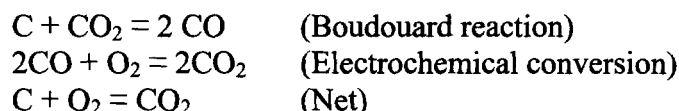
Gur and Huggins [26] also experimented with partial oxidation of elemental carbon, using oxygen transport across a thin conductive zirconia membrane, showing high efficiencies at low rates. At LLNL, we have explored dual electrolytes (zirconia and molten salt) as a means of combining the most favorable aspects of both fuel cell electrolytes [4]. Work also is reported on a Coal-fired High Temperature Fuel Cell System, in Sweden [27].

Table 5. Systems Considered in the Evaluation

No.	System diagram	Assumptions and requirements	Efficiency
1.	Electrode-grade petroleum coke ($1/GJ @$30/ton) → [diagram] Air / CO_2	1. Electrode grade petroleum, with minor alterations in thermal treatment of green coke; ash < 0.3% 2. Cell voltage = 0.8-0.85 V 3. Full utilization of C electrode	80-85% ΔH_{std}
2.	Methane ΔH_{std}= -212.8 kcal/mol ($3.50/GJ) Pyrolysis — C → Air / CO_2 — $2H_2$ → Air $CH_4 = C + 2H_2$ $\Delta H = 18$ kcal/mol 20% H_2 (unutilized)	1. Fuel cells operated at 0.86 V 2. Pyrolysis heat provided by burning unconsumed H_2 from fuel cell operating at 80% utilization 3. Pyrolysis efficiency 80% (q = 18 kcal/0.8). 4. Heat recovered from exiting gas for preheat of fuels.	67% HHV (73% LHV)
3.	$C_{10}H_{22}$ → Pyrolysis 59.67 kcal/mol 1 mol 1632.35 kcal/mol HHV (1516.6 kcal/mol LHV) — 10 C → Direct Carbon Conversion → 784.2 kcal-e / CO_2 — 11 H_2 → Fuel cell → 431.3 kcal-e / 1 H_2 — 1 H_2 → Condenser → H_2O_{liq} E = 0.85 V $\eta_u = 1.0$	1. Pyrolysis of a heavy oil (simulated for calculations as decane; $\Delta H = $ 60 kcal/mol; low ash, < 0.1% 2. Operation of fuel cells at 850 ¡C 3. Recovery of H_2 by condensation of steam 4. Full C utilization; 90% H_2 utilization, single pass, 90%. 5. Heat of CO_2 and H_2O exhaust recovered for preheat of fuels	72% HHV (77% LHV)
4.	Flue — High-T Fuel Cell NG → CH_4 Decomposer — air → Boiler → turbine NG / Molten salt C-entrained — Carbon Conversion / air	1. NG pyrolysis using NG, on molten salt substrate 2. High temperature fuel cells 3. Rankine steam cycle	75.5% HHV (83.4 % LHV)

| 5. | | 1. Hydropyrolysis of low rank coals; slip stream of H_2 converted in fuel cell.
2. High temperature fuel cells. | 69% HHV (76% LHV) |

We have included in this review the considerable amount of work done by Weaver et al. [27-29] and by Vutetakis [30,31]. These approaches clearly show the low polarization capabilities of turbostratic carbons derived from coal as well as report the full electrochemical conversion of carbon to CO_2 (4 electrons transferred per mole C). However, these researches did not circumvent the problems of ash entrainment into the fuel cell, of electrode fabrication costs, and of the logistics problems of fuel distribution. Vutetakis did not work in full C/air cells but rather conducted research on the carbon anode half-cell.
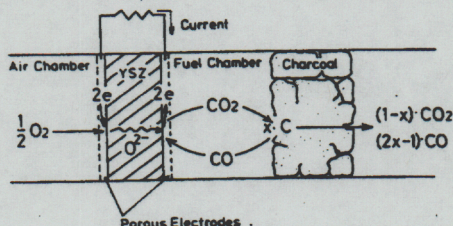

Fig. 6. Direct conversion of elemental carbon is proposed through generation of electrochemically reactive CO using the Boudouard reaction [fig. 6, ref. 25].

6. Estimates of carbon fuel and carbon cell costs

Cost of carbon and alternative fuels. Furnace blacks are produced by a long sequence of unit processes beginning with pyrolysis (using methane combined with oil-derived liquids), followed by quenching, separations, and chemical treatments, sizing, pelletizing and bagging. The reactive properties we seek are associated only with the first stage. While the finished product carbon blacks have a selling price of between about $0.22 and $0.55/lb, the first stage contributes only $0.09-0.11/lb to this price, according to industry statements. For a first stage producing the required nanostructure and feeding directly to the cell, the fuel cost is $7/GJ (based on heat of combustion of the carbon, 94.05 kcal/mol). Electrode grade petroleum cokes used in the Hall process currently cost 20-30 $/ton (~ $1/GJ) (1999 data). [Some low-sulfur, petroleum cokes now sell for 80-250$/ton. (2.69-8.40 $/GJ)]. These figures are shown in Figure 7, along with current costs of natural gas, hydrogen from steam reforming, and electrolytic hydrogen. When we factor in the energy conversion efficiencies of the respective electrochemical steps, there is a significant economic advantage of the use of carbon fuels.
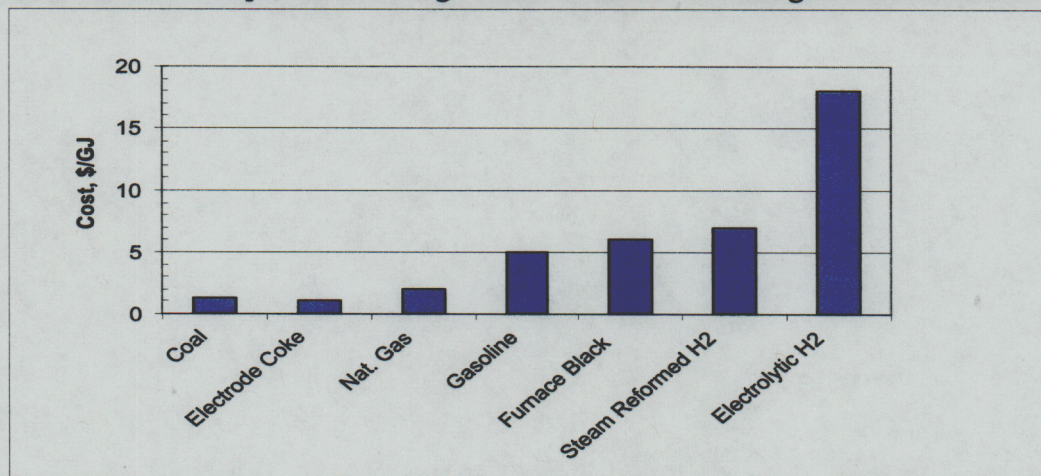

Fig. 7. Costs per unit of heating value of various fuels. [At this writing, the cost of natural gas has nearly doubled, to $7/GJ; this would shift most of these figures upward.]

Cost of Carbon Conversion Cell. In order to estimate carbon hardware costs, we offer the engineering design in Figure 8. The design was developed on the basis of procurable

components and reflects the configuration of our small test cells. The cost of the components, assembly and markets is given in Table 6.

Table 6. Cost estimates of a cell operating with procurable components at a design point of 1 kW/m²

Cost Factor	Basis	Cost, $/kW
Zirconia fabric	Zircar, Inc. quote: $200/m²	200
Nickel felt	Eltech, Inc.; quote: $20/m²; quote 10/5/98	20
Stainless steel lid	Ni plated SS frame, $5/lb	75
Graphite base and collector	$0.50/lb	20
Assembly	20% of parts	63
G&A, profit markup	20% of parts and labor	95
Total		$473
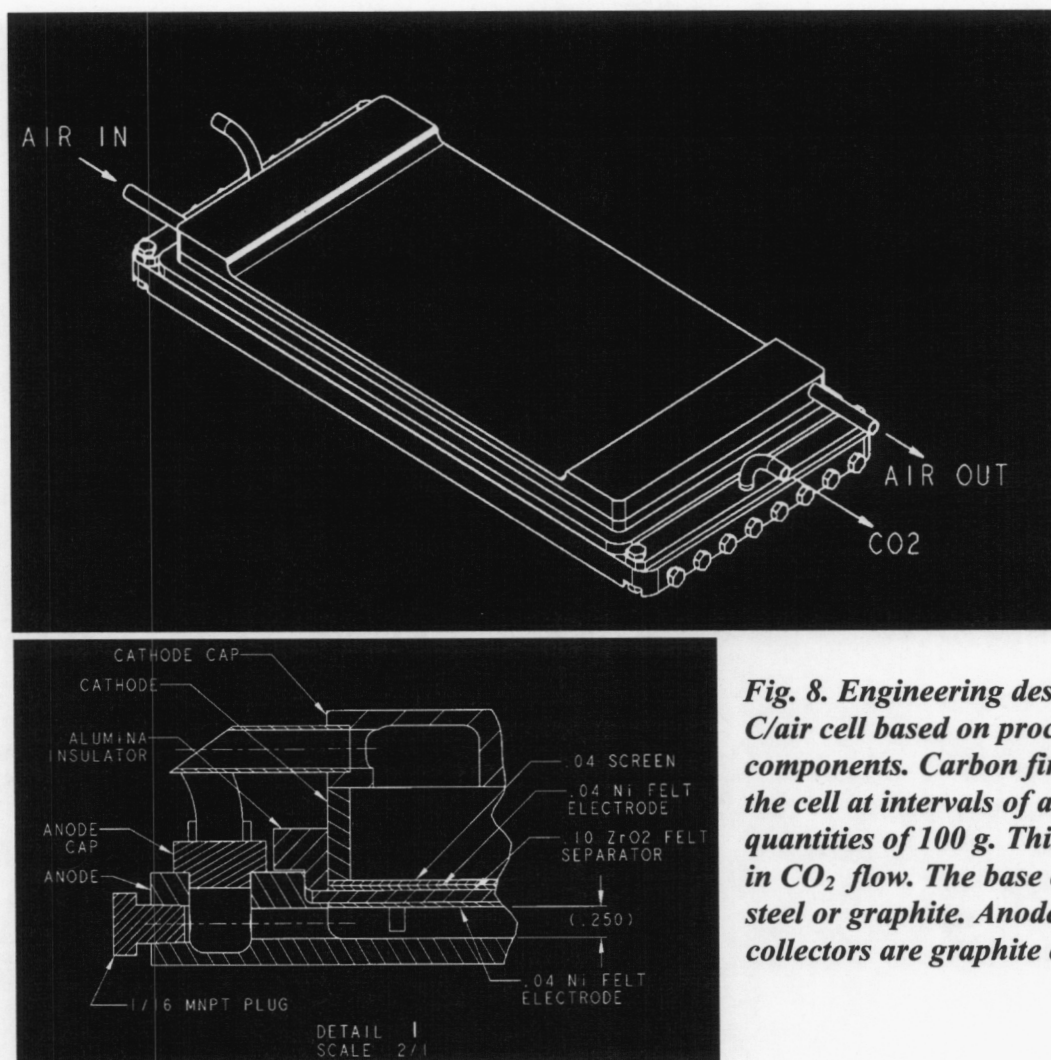
Fig. 8. Engineering design of 100 W C/air cell based on procurable components. Carbon fines are fed into the cell at intervals of about 4 days in quantities of 100 g. This is entrained in CO_2 flow. The base can be stainless steel or graphite. Anode current collectors are graphite or nickel.

7. Impact

We have attempted to estimate the potential impact of these technologies on global CO_2 emissions over time frame of 20-40 years. First, the impact on electric power generation is clear.

Regardless of the source (petroleum coke, oil, coal, natural gas), these conversion schemes entailing DCC roughly double the yield of electric power output per unit of heating value of the fossil resource, and hence halve the global carbon emissions. The projections for electric power production in 2020 and the resultant carbon emissions are given in Table 8. In the columns on the right, the decrease in carbon emissions achieved by increase of efficiency alone are compared with the additional benefits of geologic sequestration of that CO_2 emitted by the direct carbon conversion cells. If the option to sequester the CO_2 is not exercised, then the increase in CO_2 will be halved. If the option to sequester is exercised, then the emissions of CO_2 per unit of power are decreased by an order of magnitude.

Unlike combustion, the carbon cell emits a pure CO_2 byproduct that can be sequestered without any additional costs of separation or purification. Thus, the sequestration option is achieved with an absolute minimum cost both in terms of dollars and in terms of CO_2 gross production per unit of electric energy yield. We have assumed, for the moment, that the process heat for pyrolysis and carbon extraction from coal results in some CO_2 that is uneconomic to recovery from stack gases.

The unknown factor is how much electrification will occur globally. Today, nearly half of the CO_2 emissions arise from sources of combustions not related to electric power generation (1/6 of emissions), transportation or industrial thermal processes. Hence, even the elimination of CO_2 emissions from all electric power generation would have a marginal effect on curtailing emissions under the current distribution of energy use. However, we expect that increases in GNP in third world countries will be accompanied by increases in electrification, and that transportation may eventually include substantial amounts of electricity use through fuel cells or secondary batteries.

Table 8. Potential Impact of Direct Carbon Conversion Technologies on Global Increase in Carbon Emissions (million tonnes, as C) per year.

	Global Carbon Emissions, MT-C				Savings with DCC		
	MT/QBTU	2000	2020	Change	Efficiency ratio	Without Sequestration	With sequestration
Oil	17.0	247	333	86.7	1.8	48	5
NG	13.9	357	804	447.4	1.8	242	24
Coal	25.4	1422	1988	566.2	2.0	288	58
Tot		2025	3126	1100		579	87

The control of greenhouse emissions is a complex problem requiring actions on multiple fronts: conservation, reduction of non-industrial burning, electrification or CNG for transportation, non-fossil electricity production (renewable and nuclear) and shift in industrial thermal energy and residential space heating to high-hydrogen fuels e.g., natural gas.

Nevertheless, we believe there is significant value in development of a technology that doubles the yield of electric energy from each unit of fossil resource. The solution to the global problem is far more extensive, and beyond the scope of power production technology alone.

The distribution and location of fossil fuel in the world is significant (Figure 9). Ninety percent our energy used in electric power generation comes from coal, natural gas or petroleum. Coal represents 60% of the resource base and is the strongest emitter of CO_2. Despite any international agreement, coal is so extraordinarily plentiful that we can be assured that it will be burned and that the global CO_2 emissions management is correctly termed a coal utilization problem.

Eighty-one per cent of the worlds coal, and fully one-half of the fossil fuel resource base, resides within three regions: Former Soviet Union, China and US/Canada. Attempts to reduce global emissions through international cooperation would be greatly benefited by the emergence of technology providing high efficiency conversion and allowing an option for sequestration at the lowest possible cost.
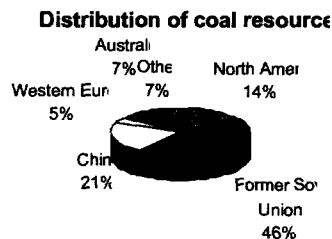
Distribution of coal resource

Australi 7% Othe
Western Eur 7% North Amer 14%
5%
Chir
21%
Former So'
Union
46%

Fig. 9. The CO_2 emissions problem can be accurately characterized as a coal problem, because of the abundance of coal and the intensity of carbon. Half the world s fossil resources are in the form of coal; of that fraction, 81% reside within North America, Former Soviet Union, and China

8. Conclusions of this Study

The conclusions of this study are as follows.

1. *Need for high efficiency conversion processes.* The curtailment of carbon dioxide emissions from fossil fuel combustion benefits from new technologies for electric power production having efficiencies well beyond the levels achieved in conventional utilities (35-40%), hydrogen fuel cells (45-55%) or advanced combined cycle plants (55%, HHV). Enhanced conversion efficiencies are particularly needed for coal, which constitutes over half of the earth s fossil fuel reserves.

2. *Carbon conversion systems.* Elemental carbon, derived from hydrocarbons by controlled pyrolysis, can be converted to electricity at efficiencies of 80-85%, at rates practical for utility application. This conversion results in a pure CO_2 byproduct suitable for sequestration without additional collection and purifications costs. The rate of the cell discharge (current density) depends critically on structure on the nanometer scale, including graphene plane spacing, and basal-plane and lateral crystallite dimensions, L_c and L_a, respectively. The slurry formed by mixing particles with molten carbonate constitutes the anode material. The air cathode is similar to that used in other high temperature fuel cells.

3. *Thermodynamic basis for efficiency of direct carbon conversion.* The direct carbon conversion cell has fundamental efficiency advantages over hydrogen as an electrochemical fuel. The theoretical efficiency ($\Delta G_T/\Delta H_{std}$) is 100.3% a consequence of the near zero entropy change of the reaction (+0.4 eu/mole). The carbon reactant and CO_2 product exist at unit activity in separate phases; this allows full utilization in single pass mode of operation, with constant and uniform current density and EMF. At 850 ¡C, direct carbon conversion has a 30% advantage in efficiency over hydrogen conversion.

4. *Reactant feed.* Pneumatic distribution of carbon is proposed, based on concurrent industry practice. At 1 kA/m^2, the rate of carbon transport is 113 g/m^2-h. The carbon/melt slurry is not explosive.

5. *Historical perspective.* Large carbon/air cells have been operated using rigid electrodes made of devolatilized coal on kW scales and at rates exceeding 1.5 kW/m^2. Primary barriers to commercial development were: exhaustion of the melt by ash entrained with the fuel; cost of anode fabrication; logistics of distribution to cell stacks; and limited supply of reactive carbons. These problems are circumvented by the current approach,

which uses carbons derived from pyrolysis of any ash-free hydrocarbon. Our approach obviates electrode fabrication by formation of slurry electrodes and uses pneumatic means for distribution to the cells.

6. *Systems for conversion of fossil fuels to reactive carbons and hydrogen.* Various grades of petroleum coke are produced as a byproduct of petroleum refining. An analysis of five routes connecting petroleum coke, refinery products, natural gas and low rank coals, with efficiencies generally above 63% HHV (corresponding to 70% LHV for methane).

7. *Costs of cell and turbostratic carbons.* Based on current cell hardware an designs, using graphite and zirconia fabric construction, cell costs are relatively low: we estimate about $500/kW. Turbostratic carbons are produced in pyrolysis unit process equipment, yielding product with reactivity dependant on operating conditions and fuel mixes. However, the cost of pyrolysis (regardless of nanostructure) is bound: 9-11 cents per pound, corresponding to about $7/GJ.

8. *Critical tasks in the development of Direct Carbon Conversion as an option for efficient power production.* Next steps in the development of this approach are:

    a. *Tests on scale.* Long-term tests should be conducted in large-scale demonstration units (~ 100-1000 W), with provisions for pneumatic feed of turbostratic carbon particulates. This will verify scale capability and fundamentals of feed.

    b. *Defining the relation between nanostructure, pyrolysis and electrochemical reactivity.* We need to understand the relation between the conditions of pyrolysis, nanostructure and electrochemical reactivity of product carbon materials. This can be done in small scale experiments using plug flow quartz pyrolysis units feeding directly into high-temperature electrochemical micro-cells, with off-line determination of crystallographic properties, particle microstructure, and related measures of chemical reactivity (air oxidation).

    c. *Determining the limits of reactivity of petroleum cokes.* Wide ranges of petroleum cokes are available having high sulfur content. The resistance of alkaline and other electrolytes to sulfur and the anodic properties of high-sulfur coke need to be measured and modeled.

    d. *Hydropyrolysis process design.* Additional industrial process data and models need to be examined to determine the range of suitable coals, yields, effects of impurities, and cost of operation.

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